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(54) Title: TANTALUM COMPOUNDS

(57) Abstract

The invention provides new tantalum compounds of the formula: $Ta(OR)_{5-n}X_n$ where n is 1, 2 or 3; each R is independently selected from a straight or branched chain alkyl group having between 1 and 4 carbon atoms, or $SiMe_3$; and X is a bidentate ligand. These compounds may be used as precursors for metal organic chemical vapour deposition (MOCVD) of oxide layers in applications such as integrated circuit dielectrics, microwaves, optical coatings and catalysts.

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TITLE: TANTALUM COMPOUNDS

FIELD OF THE INVENTION

The present invention relates to novel tantalum compounds. The compounds are for use particularly, but not exclusively, as precursors for metal organic chemical vapour deposition (MOCVD) or sol-gel processes to fabricate tantalum oxide based materials.

DESCRIPTION OF THE PRIOR ART

Tantalum oxide based materials are of potential importance as storage capacitor dielectrics in dynamic random access memory devices (DRAMs), due to their high dielectric constant (20-25 $fF/\mu m^2$) compared to conventional SiN/SiO_2 (6-9 $fF/\mu m^2$) devices and also as a gate insulator in metal oxide semiconductor (MOS) devices as applied to VLSI microcircuits. With increasing miniaturisation conventional insulator films are approaching thicknesses at which direct electron tunnelling becomes significant. The introduction of a new insulator with a higher dielectric constant is an effective approach to counteracting this problem.

The major foreseeable application of tantalum based molecular precursors is in the synthesis of electroceramics, e.g. ceramic thin or thick films for use in electronic devices such as VLSI microcircuits or dielectric films; see Lane, Chen, Sandler, Freeman and Page, Mater. Res. Soc., Symp. Proc. 1992, **250**, 331-336; storage dielectric films in 64 MBit DRAM's; see Shibuya, Kitagawa, Kamata and Hirao, Jpn. Pat. 93,221,644 filed 13th February 1992; piezoelectrics such a $LaCuO_2$; H. Müller-Buschbaum, Agnew. Chem. 1989, **28**, 1472-74;

ferroelectrics, i.e. $KTaO_3$ and K_2TaNbO_6, see E. Wu, K.C. Chen, J.D. Mackenzie, In Better Ceramics through Chemistry, C.J. Brinker, D.E. Clark, D.R. Ulrich, Eds., North-Holland, New York, 1984, pg 169; piezoelectrics, ie. $PbSc_{0.5}Ta_{0.5}O_3$ and $ScTaO_4$ and dielectric layers and anti-reflectance coatings, ie. optics.

Chemical vapour deposition (MOCVD) is an excellent technique for preparing conformal coatings because step coverage is very important in three dimensional memory cells. Selection of the source material is important in optimising the deposition rate and film quality, see gQ. Lo, D-L Kwong, P.C. Fazan, V.K. Mathews and N. Sandler, IEEE Electronic Device Letters, 1993, **14**, 216-218 and references therein. For such chemicals to find ready application, they should be stable in the vapour phase, with a significant vapour pressure at 100°C and have excellent mass transport properties, thereby allowing the formation of a thin or thick film of tantalum oxide (Ta_2O_5) to be deposited onto the desired substrate, see for example, S. Zaima, T. Futura, Y.Yasada, M. Ida, J. Electrchem Soc., 1990, **137**, 1297-1300.

Metal oxide based ceramic materials are normally made by classical "heat and bake" technology; see D. Segal, Chemical Synthesis of Advanced Ceramic Materials, Cambridge University Press, Cambridge, 1991. This approach relies upon the intimate mixing of metal-oxygen based materials (e.g. metal carbonates, nitrates and hydroxides) via the use of techniques such as ball-milling, fusion processes, and uniaxial or hot isostatic pressing. Although these processes are attractive owing to their inherent simplicity and low cost, there are several inherent disadvantages. These are high temperature processing and post-annealing under a flow of

oxygen gas, which would ensure that any meta-stable phases could not be accessed by this approach. There is also the added difficulty of phase inhomogeneity, for example tetragonal and orthorhombic forms present in the same material and also the presence of ionic impurities, which are frequently found at the grain boundaries. If high purity is required, then extensive chemical pretreatment of the raw materials is required, and even then the purity levels still fall far short of those obtainable by other methods. Thus the quality of films produced is highly dependent on achieving the correct stoichiometry, producing highly oriented films and avoiding substrate/film interactions.

An alternative strategy involves the use of metal alkoxides or ß-diketonates. These compounds are readily obtained as either crystalline solids of known stoichiometry or distillable liquids obtainable in high purity, with excellent solubility in organics solvents, long term stability in an inert atmosphere, and are sufficiently reactive that most reactions occur at or near room temperature. Most importantly by using such materials fine control of molecular stoichiometry is possible and access to previously unobtainable metastable phases is achievable. These materials find extensive use in either sol-gel or chemical vapour deposition (MOCVD) processes, which involve the formation of either thick films (sol-gel spin coating); see C.J. Brinker, A.J. Hurd, P.R. Schunk, gC. Frye and C.S. Ashley, J. Non-Cryst. Solids 1992, **147**, 424-436, C. Sanchez and M. In, J. Non-Cryst. Solids, 1992, **147**, 1-12; or alternatively ultrathin films (20 Å or less) for optical or microelectronic applications by MOCVD. The nature of these processes allows compositional control of the concentration of both dopants and the deposition rate of the metal oxide film. The most

important requirement is the physical state of the precursor and its associated vapour pressure. In order to maintain a constant delivery of precursor by the carrier gas (for example N_2), the condition of saturation equilibrium must be uniform throughout the growth run period. This important parameter is best catered for by a liquid source which distils with minimal decomposition when a carrier gas is bubbled through the heated material.

Tantalum ethoxide has been traditionally viewed as the precursor of choice, see for example laser MOCVD of tantalum oxide, Nishimura, Tokunmura and Tsuji, Thin Solid Films, 1993, 26, 144-148, Availability has played a dominant role in its selection because other compounds have been reported and several with reportedly higher volatilities, but because they are poorly characterised, their modes of decomposition have remained unstudied.

Conventional tantalum precursors for metal oxide films have several drawbacks, most notably in the high residue left in commercial evaporators/bubblers for MOCVD and also poor stability in the atmosphere. The use of fluorinated beta-diketone precursors would result in the formation of TaF_5, which has to be removed with either superheated water vapour or air at elevated temperature to yield the required oxide based film. Therefore, to produce epitaxial or high quality films it is important to avoid the use of fluoride based compounds, even though such complexes may have excellent vapour pressure and mass transport properties. Thus, as stated above, a precursor is required that vaporises without significant decomposition and remains intact in the vapour phase for considerable time periods, ie. for at least the length of time of the MOCVD experiment. In order to maintain a constant flux of chemical delivery by a carrier gas to the substrate, the

condition of saturation equilibrium must be uniformly maintained through growth run-time. This is best achieved in a liquid source by bubbling the carrier gas through the heated compounds. This technique is important because of the potential for large area film growth that it offers, with precise control of thickness (deposition rate) and also allowing for the deposition of multi-layer structures and control of microstructure and composition; see M.L. Hitchman, D.D. Gilliland, D.J. Cole-Hamilton and S.C. Thompson, Inst. Phys. Conf. Serv., 1990, **305**, 111.

Tantalum metal alkoxides are well established materials; see D.C. Bradley, B.N. Chakravarti and W. Wardlaw, J. Chem. Soc. A, 1956, 2381-2384; R.C. Mehrotra et.al., "Metal Beta-Diketones", Academic Press, London, 1978 and H. Okamura and H.K. Bowen, Ceramics Intl. 1986, **12**, 161-171 for preparative details from their chlorides in alcohol with ammonia. A considerable degree of diversity has been previously found in their chemistry, notably with differing alkoxide groups. Classical studies by Bradley et.al. in 1956 (see pg.2) demonstrated the dramatic effect of the size and branching of an alkyl group on volatility. Lewis based adducts of tantalum alkoxides have also been reported, such as the dimeric crystalline complex $Ta_2(OPr^i)_{10}(NH_2CH_2CH_2NH_2)]$, see M.S. Bains and D.C. Bradley,Can. J. Chem., 1962, **40**, 2218-2228.

The most commonly used strategies for preparing volatile precursors are the use of bulky or alternative fluorinated ligands that encapsulate the metal ions, and thus create discrete molecular species. This phenomenon occurs due to reduced intermolecular associations between metal centres, and therefore changes the orientation of the packing in the solid or liquid states, this in turn gives rise to enhanced thermal and mass transport properties. This

approach has been adopted for lanthanide complexes; see W.J. Evans, J.M. Olofson, J.W. Ziller, Ingor Chem., 1989, 28, 4308, and R.E. Silvers, Science, 1978, 201, 217-223. Prior researchers have also studied the reaction of tantalum alkoxides with beta-diketones, but obtained poorly characterised, involatile materials of ill-defined stoichiometry, see P.N. Kapoor and R.C. Mehrotra, J. Less-Comm. Met., 1965, 8, 399-346. This work therefore did not produce materials of utility for MOCVD.

Due to its large ionic radii and moderate coordination number, tantalum is rather difficult to coordinatively saturate to yield monomeric complexes. Bulky ligands are limited in their ability to coordinatively saturate this metal. Poly-functionalised ligands have been extensively used for other metals, but to date have not been reported for tantalum; see O. Poncolet and K.G. Hubert-Pfalzgraf J. Chem. Soc., Chem. Commun., 1989, 1846-47; and also O. Poncolet et. al. Inorg. Chem., 1990, 29, 2885-2890. there are also other complexes which contain simple ligands (for example MeO- and Pr^nO-), which are not sufficiently electron rich to supply the electronic and steric requirements of this metal. At its logical extreme this can lead to highly associated or indeed polymeric complexes, where the ligand is MeO- or EtO-. To date, there has been little success at controlling the degree of oligomerisation of tantalum based molecular precursors by tailoring the ligands to control the degradation process and thus to prevent retention of impurities (mostly carbon) in the films. Knowledge of the decomposition pathways should provide useful information for the design of precursors since attention has to be paid not only to volatility, but also to the necessity of incorporating substituents which are prone to facile hydrocarbon elimination.

Prior art has shown that there are a number of synthetic strategies which may be employed to prepare complexes and the most common route uses the well known ammonia method of Bradley et.al. (see above). These previously known precursor syntheses reveal limited systematic control of oligomer size which results in poorly characterised materials with limited moisture and thermal stability (especially at elevated temperatures where decomposition may occur resulting in the formation of non-volatile material) and a poor shelf life with a variable nature of the metal oxide film resulting. It is therefore desirable to design and synthesise thermally stable and volatile materials which will be suitable for MOCVD applications. For such compounds their volatility is mainly governed by the steric bulk of the ligand; see for example the application as a MOCVD source of $Ta(OEt)_5$, C.C. Wang, K.H. Zaninger and M.T. Duffy, RCA Rev., 1970, 31, 728 and also in the formation of $PbSc_0Ta_{0.5}O_3$ and $ScTaO_4$ polycrystalline films.

More recently $Ta(NMe_2)_5$ has found application as a tantalum oxide source. This material is chemically stable up to approximately 150°C and vaporises at 80°C. The films were deposited at a greater rate than is possible with $Ta(OEt)_5$ using low pressure MOCVD at temperatures of 380 - 520°. The as-deposited films were oxygen poor, however, and required considerable annealing in an oxygen atmosphere to improve the stoichiometry and reduce the leakage current to an acceptable level (see T. Tabuchi, Y. Sawado, K. Uematsu and S. Koshiba, Jap. J. Appl. Phys., 1991, **30**, L1974-1977).

The complexes for this purpose (ie. advanced tantalum precursor chemicals), must preferably satisfy the following physical and chemical criteria:

- well defined identity in either the solid state, solution or the gas phase.
- improved air and moisture stability for ease of handling.
- either low melting solids or liquids for use in conventional MOCVD bubbler source chambers.
- good solubility in a wide range of organic solvents.
- significant volatility at low temperature (less than around 160°C).

The present invention provides chemical precursor materials meeting the majority of the above requirements. We have achieved an advantage by satisfying the coordination requirements of the tantalum metal ion through a new synthesis procedure involving the use of one or more bidentate ligands.

The compounds of this invention can be used as precursors for the deposition of tantalum oxide layers by MOCVD. Tantalum oxide is employed alone or in conjunction with other metal oxides as ceramic or glass layers in a range of established and emerging materials technologies such as storage capacitor dielectrics (DRAM), piezoelectrics, microcircuits, dielectrics layers, anti-reflectance coatings and optoelectronics. The reliable availability of properly characterised precursor chemicals plays a key role in technological development that enables devices to be manufactured for the use in information technology, medical instrumentation and energy conservation.

The above technical documents are incorporated herein by reference.

SUMMARY OF THE INVENTION

According to the present invention there is provided a compound of the formula $Ta(OR)_{5-n}X_n]$, wherein:

n is 1, 2 or 3;

each R is independently selected from a straight or branched chain alkyl group having between 1 and 4 carbon atoms, or $SiMe_3$; and

X is a bidentate ligand.

For MOCVD application the distillation temperature of the compound preferably does not exceed 160°C at a pressure of 0.1 mm Hg.

The term "distillation temperature" is used herein to refer to the head temperature, ie the measured temperature of the vapour prior to condensing.

The bidentate ligand X is preferably selected from the following:

the residue of an alkoxy-alcohol of formula $(R(OCH_2CH_2)_nOH$ where R is straight or branched C_{1-4}alkyl, and n=1 or 2;

the residue of an amino-alcohol $R^iR^{ii}NCH_2CHR^{iii}OH$, where R^i, R^{ii} and R^{iii} are each independently selected from hydrogen, and straight or branched C_{1-4}alkyl;

a beta-dicarbonyl anion derived from a compound of formula $R^iR^{ii}R^{iii}$ $CCOCHR^{iv}COR^v$, where R^i,R^{ii},R^{iii}, R^{iv} and R^v are independently selected from hydrogen, C_{1-4}alkyl, optionally substituted by fluorine or phenyl, and R^v may also be an alkoxy residue containing 1 to 6 carbon atoms.

Although each R group may be different, such pure materials are relatively difficult to prepare and characterise. It is therefore preferred that each R group has the same structure in a given compound, thereby simplifying its preparation and characterisation.

It is particularly preferred that R is selected from: methyl, ethyl, isopropyl, or t-butyl, as these materials are particularly stable under the reaction and distillation conditions.

The compounds will be referred to as follows: n = 1 (Type I complex), n=2 (Type II Complex) and n=3 (Type III complex).

Type I structure: eg $Ta(OEt)_4X$ is monomeric, with the tantalum atom binding to all four monodentate alkoxide ligands and also to the bidentate ligand, e.g. dimethylamino-alcohol, beta-diketone, alkoxy-ethanol etc). Thus the tantalum atom adopts a six-coordinate geometry, with essentially regular octahedral geometry. A study of a space-filling model of this complex indicates that the ligands are uniformly distributed around the metal centre. The coordination of an additional amino-nitrogen centre is less favourable due to the presence of the five tightly held alkoxide and amino-alkoxide ligands, effectively creating a uniform coordination sphere around the tantalum centre.

Type II structure: eg $Ta(OEt)_3X_2$ consists of a tantalum centre coordinated to three alkoxide ligands and to two bidentate functionalised ligands, (e.g. dimethylaminoalcohol, betadiketone, methoxyethanol etc. The metal centre is therefore seven coordinate

with the overall coordinating polyhedron being best described as distorted capped octahedral. This structure allows the utilisation of an additional binding site on the metal, but at the expense of stereochemical stability, which is reflected in the vapour pressure and thermal stability data.

Type III structure: eg $Ta(OEt)_2X_3$ consists of a tantalum centre coordinated to only two ethoxide ligands and to three bidentate beta-diketone ligands. The metal centre is thus eight coordinate with the overall coordination polyhedron being best described as distorted square anti-prismatic. The structure allows the utilisation of all possible binding sites on the metal, but at the expense of thermal stability, which is reflected in the relatively poor vapour pressure data and relatively low yield of material obtainable on high vacuum distillation.

The coordination numbers of the metals in these complexes are six, seven or eight, with six being the most stable which is in accord with the earlier work of H. Funk, Beriche, 1934, **67B**, 1801 and is the principal reason for the beneficial chemical and physical properties of the compounds (Table 1). Thermal behaviour has been studied by high vacuum distillation behaviour and clearly reveals that the materials containing only one chelating X ligand are the most volatile, e.g. $Ta(OEt)_4OCH_2CH_2NMe_2$ and $Ta(OEt)_4OCHMeCH_2NMe_2$. These two complexes distil quantitatively around 85°C at 0.1 mm pressure. In order to compare the steric effects of the alkyl chain, the complex $Ta(OEt)_4OCH_2CH_2CH_2NMe_2$ was synthesised. This material has a higher distillation temperature of 122°C at 0.08 mm Hg. Therefore steric effects have a greater contributory effect to the complex stability than does the six-members

chelate effect, which presumably in this case is destabilised to some extent. The effects of R' group size were also studied on the X ligand and the methyl group was found to be the optimum size to ensure total saturation of the tantalum metal centre and to create a thermally stable complex.

It is therefore preferred that n=1, because of the particularly low distillation temperatures which may be achieved for such materials.

The attached Table 1 gives exemplary physical properties of the compounds of this invention.

These compounds all have excellent solubility in a wide range of organic solvents, for example: n-pentane, hexane and heptane; benzene, toluene and xylene; diethyl ether, tetrahydrofuran, di-n-butyl ether, dimethylsulphoxide, acetonitrile, pyridine and chloroform. Indeed, the outstanding solubility shown by the majority of these complexes ensures that they do not crystallise out of organic solvents. If desired in a crystalline form, then most or all of the organic solvent must be removed and the compound in certain cases may be crystallised from the oily materials remaining.

The excellent solubility of these new compounds in organic solvents makes them eminently suitable for use in a wide range of applications, for example MOCVD, and as potential sol-gel precursors.

The materials stated in the prior art to have formulae such as "$Ta(OR)_5$" have been shown by Bradley, Wardlaw and Whitely (JCS 1955 726) to be dimeric in nature. Unless strictly anhydrous conditions are maintained during

preparation they may be heavily contaminated with hydrated species which behave unpredictably due to intramolecular hydrolysis when heated in their vacuum evaporation points. In general the rate of evaporation of the prior art compounds declines with time and source chambers become clogged with residue.

These complexes have all been further characterised by infrared spectrometry and bands at 2900±40 are due to υ(C-H) stretching in the various alkyl groups. Peaks at 1610±8 cm^{-1} have been assigned to υ(C---O) stretch modes, and bands at 1578±8 and 1505±10 cm^{-1} to the υ(C---O) stretching modes. They also show a strong band near 1070±25 cm^{-1} which may be assigned to υ_{as}(C-O) arising from the alkoxy groups of the amino-alcohols.

A major reason for the polymerisation and presence of hydration or even halide impurities in the prior art materials was the absence of a detailed and comprehensive understanding of the control of the ligand coordination sphere around the tantalum metal centre. The compounds described in this invention have a carefully chosen mixture of ligands in the metal ion first coordination sphere. These comprise monodentate ligands based on alkoxide groups and chelating beta-diketones or functionalised alcohol residues with pendent Lewis base groups, ie. amino nitrogen or alkoxy oxygen. The outermost coordination shells of these tantalum based materials comprises hydrocarbon groups whose neighbour interactions are weak Van der Waals attractions. Thus, the molecules of this invention have little tendency to associate, and consequently have low melting points or are liquids at room temperature.

Additionally, the functionalities in the compounds of this invention in the vapour phase (see Table 1) may assist vapour phase deposition by providing an activated species such as "-$Ta(OR)_3X$" which may attach itself to the substrate surface prior to the final conversion to the metal oxide.

The absence of water or any halide impurities in the subject materials is of paramount importance. Anhydrous synthesis routes I and II employ either the metal amide or alkoxide starting materials dissolved in hydrocarbon solvent and give excellent yields.

Synthesis route I conducted in hydrocarbon solvent:

$Ta(NR_2)_5$ + 5-n ROH + n X-H ---------> $Ta(OR)_{5-n}X_n$ + 5 R_2NH

Where preferably R = Et, Pr^i or $SiMe^3$, and X is as defined above.

Synthesis route II conducted in hydrocarbon solvent:

$Ta(OR)_5$ + n X-H ---------> $Ta(OR)_{5-n}X_n$ + n ROH

Where R = Pr^i or Bu^t as the preferred alkyl groups, but other R groups as hereinbefore defined may be used.

The prime requirements for the compound is a vapour pressure high enough to allow good deposition rates, and a suitable decomposition mechanism to allow the ligands to be removed, resulting in a carbon free film.

In the compounds of this invention the tantalum metal centre is coordinatively saturated with the combined use of alkoxide groups and a chelating type of ligand e.g.

beta-diketone or functionalised alcohol. This point is of importance and presumably gives rise to their exceptional thermal stability in the vapour phase of complexes such as $Ta(OEt)_4OCH_2CH_2NMe_2$, since the chelating ligands are less readily hydrolysed than monodentate ligands. Secondly, the application of chelating ligands has reduced the possibility of interactions between the molecules, which therefore exist as monomers, thereby reducing the reducing the effective molecular mass and increasing the volatility relative to dimeric or oligomeric species. Thus hard Lewis bases (either O- or N- based) on the terminus of alcohol ligands can utilise the entropic advantages of the chelate effect and facilitate the preparation of volatile tantalum complexes via a low cost route.

The following abbreviations and chemical formula are used herein :

	methoxyethanol	$MeOCH_2CH_2OH$
	ethoxyethanol	$EtOCH_2CH_2OH$
	n-butoxyethoxyethanol	$BuOCH_2CH_2OCH_2CH_2OH$
	methylaminoethanol	$MeHNCH_2CH_2OH$
	ethylaminoethanol	$EtHNCH_2CH_2OH$
	dimethylaminoethanol	$Me_2NCH_2CH_2OH$
	diethylaminoethanol	$Et_2NCH_2CH_2OH$
	dimethylaminopropanol	$Me_2NCH_2CH_2CH_2OH$
	dimethylaminopropan-2-ol	$Me_2NCH_2CHMeOH$
acac	acetylacetonate	MeCOCHCOMe
thd	tetramethylheptanedionate	$Me_3CCOCHCOCMe_3$
tfa	trifluoroacetylacetonate	$F_3CCOCHCOMe$
hfa	hexafluoroacetylacetonate	$F_3CCOCHCOCF_3$

Me = methyl, Et = ethyl, Pr = n-propyl, Pr^i = isopropyl, Bu = n-butyl; Bu^t = tertiary butyl.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

1. TANTALUM TETRAETHOXIDE METHOXYETHOXIDE $Ta(OEt)_4OCH_2CH_2OMe$

Into a 2 litre 3 necked round bottomed flask pour under nitrogen, tantalum ethoxide (50 g 0.123 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then methoxyethanol (9.1 g, 0.123 mmole) was added via a dropping funnel to the rapidly stirring solution. After completing the addition the solution is stirred for a further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a pale yellow liquid. This material was then distilled under high vacuum, and distilled at 138-140°C at 0.1 mm Hg (head temp.) and oil bath temperature of 163-185°C to produce a clear colourless liquid. Yield of $Ta(OEt)_4OCH_2CH_2OMe$ is 43 g, 79%.
Solvent solubility: n=hexane or pentane is 600 g/l, ethanol is 1000 g/l and toluene is 350 g/l.
Molecular complexity in benzene yields a molecular weight of 420±30 (calc. 441) for a monomer.

2. TANTALUM TETRAETHOXIDE n-BUTOXYETHOXYETHOXIDE $Ta(OEt)_4OCH_2CH_2OCH_2CH_2OBu$

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (50 g 0.123 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then n-butoxyethoxyethanol (20.5 g, 0.123 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a

further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a clear colourless liquid. This material was then distilled under high vacuum and distilled at 160-162°C at 0.15 mm Hg (head temp.) and oil bath temperature of 205-220°C to produce a clear colourless liquid. Yield of $Ta(OEt)_4OCH_2CH_2OCH_2CH_2OBu$ is 17 g, 27%.

Solvent solubility: n-hexane or pentane is 650 g/l, ethanol is 1000 g/l and toluene is 400 g/l.

Molecular complexity in benzene yields a molecular weight of 495±55 (calc. 537) for a monomer.

3. **TANTALUM TETRAETHOXIDE METHYLAMINOETHOXIDE $Ta(OEt)_4OCH_2CH_2NHMe$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (46 g 0.113 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then methylaminoethanol (9.1 g, 0.113 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a pale yellow-orange liquid. This material was then distilled under high vacuum, and distilled at 119°C at 0.1 mm Hg (head temp.) and oil bath temperature of 155-165°C to produce a pale-yellow liquid. Yield of $Ta(OEt)_4OCH_2CH_2NHMe$ is 42 g, 86%.

Solvent solubility: n-hexane or pentane is 540 g/l, ethanol is 750 g/l and toluene is 300 g/l.

Molecular complexity in benzene yields a molecular weight of 425±27 (calc. 440) for a monomer

4. **TANTALUM TETRAETHOXIDE ETHYLAMINOETHOXIDE $Ta(OEt)_4OCH_2CH_2NHEt$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (50 g 0.123 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then ethylaminoethanol (12.0 g, 0.123 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a further 30 minutes. the solvent and liberated ethanol were removed under vacuum to yield a pale yellow liquid. This material was then distilled under high vacuum, and distilled at 124°C at 0.1 mm Hg (head temp.) and oil bath temperature of 155-170°C to produce a clear colourless liquid. Yield of $Ta(OEt)_4OCH_2CH_2NHEt$ is 41.8 g, 76%. Solvent solubility: n-hexane or pentane is 500 g/l, ethanol is 720 g/l and toluene is 330 g/l. Molecular complexity in benzene yields a molecular weight of 440±32 (calc. 454) for a monomer.

5. **TANTALUM TETRAETHOXIDE DIMETHYLAMINOETHOXIDE $Ta(OEt)_4OCH_2CH_2NMe_2$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (102 g, 0.251 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. then dimethylaminoethanol (25.2 g, 0.251 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a further 30 minutes. the solvent and liberated ethanol were removed under vacuum to yield a deep yellow-range liquid.

This material was then distilled under high vacuum, and distilled at 85-88 at 0.15 mm Hg (head temp.) and oil bath temperature of 120-130°C to produce a clear colourless liquid. Yield of $Ta(OEt)_4OCH_2CH_2NMe_2$ is 102 g, 91%.

6. **TANTALUM TRIS-ETHOXIDE BIS-DIMETHYLAMINOETHOXIDE $Ta(OEt)_3(OCH_2CH_2NMe_2)_2$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (49 g, 0.121 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then dimethylaminoethanol (24.2 g, 0.242 mmole), was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a pale red-orange liquid. This material was then distilled under high vacuum, and distilled at 129°C at 0.12 mm Hg (head temp.) and oil bath temperature of 160 - 180°C to produce a colourless liquid. Yield of $Ta(OEt)_3(OCH_2CH_2NMe_2)_2$ is 34 g, 50%.
Solvent solubility: n-hexane or pentane is 540 g/l, ethanol is 750 g/l and toluene is 300 g/l.
Molecular complexity in benzene yields a molecular weight of 425±27 (calc. 440) for a monomer.

7. **TANTALUM TETRAETHOXIDE DIETHYLAMINOETHOXIDE $Ta(OEt)_4OCH_2CH_2NEt_2$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (100 g 0.246 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then

diethylaminoethanol (32.5 g, 0.246 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution was stirred for a further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a pale yellow liquid. This materials was then distilled under high vacuum, and distilled at 151°C at 0.1 mm Hg (head temp.) and oil bath temperature of 180-205°C to produce a pale-yellow liquid. Yield of $Ta(OEt)_4OCH_2CH_2NEt_2$ is 84 g, 69%.
Solvent solubility: n-hexane or pentane is 580 g/l, ethanol is 800 g/l and toluene is 350 g/l.
Molecular complexity in benzene yields a molecular weight of 460±25 (calc. 482) for a monomer.

8. TANTALUM TETRAETHOXIDE DIMETHYLAMINO-2-PROPOXIDE $Ta(OEt)_4OCHMeCH_2NMe_2$

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (50 g, 0.122 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then dimethylaminopropan-2-ol (15.0 g, 0.122 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution was stirred for a further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a pale yellow liquid. This material was then distilled under high vacuum, and distilled at 81-84°C at 0.10 mm Hg (head temp.) and oil bath temperature of 122-135°C to produce a colourless clear liquid. Yield of $Ta(OEt)_4OCHMeCH_2NMe_2$ is 39 g, 70%.
Solvent solubility: n-hexane or pentane is 440 g/l, ethanol is 620 g/l and toluene is 400 g/l.
Molecular complexity in benzene yields a molecular weight of 450±30 (calc. 467) for a monomer.

9. **TANTALUM TETRAETHOXIDE DIMETHYLAMINOPROPOXIDE $Ta(OEt)_4OCH_2CH_2CH_2NMe_2$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (50 g, 0.122 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then diemethylaminopropanol (14.4 g, 0.122 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution was stirred for a further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a colourless liquid. This material was then distilled under high vacuum, and distilled at 122°C at 0.08 mm Hg (head temp.) and oil bath temperature of 163-185°C to produce a clear colourless liquid. Yield of $Ta(OEt)_4OCH_2CH_2CH_2NMe_2$ is 35 g, 72%. Solvent solubility: n-hexane or pentane is 480 g/l, ethanol is 650 g/l and toluene is 360 g/l. Molecular complexity in benzene yields a molecular weight of 455±20 (calc. 467) for a monomer.

10. **TANTALUM TETRAETHOXIDE ACETYLACETONATE $Ta(OEt)_4MeCOCHCOMe$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (50 g, 0.122 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then acetylacetone (12 g, 0.122 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution was stirred for a further 30 minutes. The solvent and liberated ethanol were removed under vacuum to yield a pale yellow liquid. This material

was then distilled under high vacuum, and distilled at 112°C at 0.8 mm Hg (head temp.) and oil bath temperature of 147-160°C to produce a clear colourless liquid, which sets on cooling to yield a colourless solid. Yield of $Ta(OEt)_4MeCOCHCOMe$ is 45 g, 80%.
Solvent solubility: n-hexane or pentane is 400 g/l, ethanol is 360 g/l and toluene is 250 g/l.
Molecular complexity in benzene yields a molecular weight of 448±30 (calc. 464) for a monomer.

11. **TANTALUM BIS-ETHOXIDE TRIS-ACETYLACETONATE $Ta(OEt)_2(MeCOCHCOMe)_3$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum ethoxide (75 g, 0.814 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum ethoxide. Then acetylacetone (55 g, 0.552 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a further 45 minutes. The solvent and liberated ethanol were removed under vacuum to yield an orange-red liquid which crystallises over a period of 12 hours. This materials was then distilled under high vacuum, and distilled at 95-100°C at 0.10 mm Hg (head temp.) and oil bath temperature of 137-149°C to produce a red-orange liquid (crystallises <36°C). Yield of $Ta(OEt)_2(MeCOCHCOMe)_3$ is 58 g, 56%.
Solvent solubility: n-hexane or pentane is 730 g/l, ethanol is 600 g/l and toluene is 450 g/l.
Molecular complexity in benzene yields a molecular weight of 540±43 (calc. 570) for a monomer.

12. **TANTALUM TETRA-T-BUTOXIDE ACETYLACETONATE $Ta(OBu^t)_4MeCOCHCOMe$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum tert-butoxide (40 g, 0.073 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum tert-butoxide. Then acetylacetone (7.2 g, 0.072 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution was stirred for a further 45 minutes. The solvent and liberated ethanol were removed under vacuum to yield a yellow-red solid. This material was then distilled under high vacuum, and distilled at 103°C at 0.15 mm Hg (head temp.) and oil bath temperature of 134-147°C to produce an orange solid (MP 34°C). Yield of $Ta(OBu^t)_4MeCOCHCOMe$ is 33 g, 80%.
Solvent solubility: n-hexane or pentane is 480 g/l, ethanol is 500 g/l and toluene is 410 g/l.
Molecular complexity in benzene yields a molecular weight of 560±33 (calc. 572) for a monomer.

13. **TANTALUM TRIS-T-BUTOXIDE BIS-ACETYLACETONATE $Ta(OBu^t)_3(MeCOCHCOMe)_2$**

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum tert-butoxide (40 g, 0.073 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum tert-butoxide. Then acetylacetone (14.4 g, 0.144 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a further 45 minutes. The solvent was removed under vacuum to yield a yellow liquid. This material was then distilled

under high vacuum, and distilled at 88°C at 0.10 mm Hg (head temp.) and oil bath temperature of 118-130°C to produce a pale-yellow liquid. Yield of $Ta(OBu^t)_3(MeCOCHCOMe)_2$ is 30 g, 69%.
Solvent solubility: n-hexane or pentane is 670 g/l, ethanol is 400 g/l and toluene is 390 g/l.
Molecular complexity in benzene yields a molecular of 565±45 (calc. 598) for a monomer.

14. TANTALUM BIS-T-BUTOXIDE TRIS-ACETYLACETONATE $Ta(OBu^t)_2(MeCOCHCOMe)_3$

Into a 2 litre 3 necked round bottomed flask was poured under nitrogen, tantalum tert-butoxide (40 g, 0.073 mole) and n-hexane (250 ml). An overhead mechanical stirrer was attached and the solution stirred for 5 minutes to ensure complete dissolution of the tantalum tert-butoxide. Then acetylacetone (21.6 g, 0.216 mmole) was added via a dropping funnel to the rapidly stirred solution. After completing the addition the solution is stirred for a further 45 minutes. The solvent was removed under vacuum to yield an orange liquid. This material was then distilled under high vacuum and distilled at 98-100°C at 0.10 mm Hg (head temp.) and oil bath temperature of 135-145°C to produce a red-orange liquid. Yield of $Ta(OBu^t)_2(MeCOCHCOMe)_3$ is 21.5 g, 45%.
Solvent Solubility: n-hexane or pentane is 630 g/l, ethanol is 370 g/l and toluene is 490 g/l.
Molecular complexity in benzene yields a molecular weight of 590±55 (calc. 624) for a monomer.

15 **TANTALUM TETRAMETHOXY DIMETHYLAMINOETHOXIDE**
$Ta(OMe)_4OCH_2CH_2NMe_2$

Into a 1 litre 3 necked round bottomed flask was poured under nitrogen a solution of 84 g (0.025 mole) tantalum methoxide in 250 ml hexane. The solution was stirred for 5 minutes to ensure uniform distribution of the tantalum methoxide then 22.25 g (0.25 mole) of dried dimethylaminoethanol was added via a dropping funnel to the rapidly stirred solution. Stirring was continued for a further 30 minutes. The solvent and liberated methanol were removed under vacuum to yield an orange liquid which was purified by vacuum distillation at 90° head temperature and 0.2 mm Hg with an oil bath temperature of 125° to produce a clear colourless liquid weighing 87 g (88.5% yield).

16 **TANTALUM TETRAKIS-TRIMETHYLSILOXY ACETYLACETONATE**
$Ta(OSiMe_3)_4MeCOCHCOMe$

Into a 1 litre 3 necked round bottomed flask was poured under nitrogen a solution of 150 g (0.24 mole) of tantalum trimethylsiloxide in 500 ml hexane. The solution was stirred for 5 minutes to ensure dissolution then 24 g (0.24 mole) of dried acetylacetone was added via a dropping funnel to the rapidly stirred solution. Stirring was continued for 30 minutes. The solvent and liberated by-products were removed under vacuum to yield a yellow liquid which was purified by vacuum distillation at 100°C head temperature and 0.1 mm Hg with an oil bath temperature of 135° to produce a colourless liquid weighing 130 g (85% yield). This material was thermally stable at 300°C.

Table 1 Physical properties of selected complexes

	mp/ °C	Dist temp/ °C (mm Hg)	Density	Yield /%	Appearance	Decompn	Shelf Life
$Ta(OEt)_5$	21	146 (0.15)	1.56	> 90	colourless liquid	None	Excellent
$Ta(OEt)_4OCH_2CH_2OMe$	-	138 (0.10)	-	79	colourless liquid	None	Good
$Ta(OEt)_4(OCH_2CH_2)_2OBu$	-	160 (0.10)	-	27	colourless liquid	Substantial	Poor
$Ta(OEt)_4OCH_2CH_2NHMe$	-	119 (0.05)	-	86	yellow liquid	Minor	Good
$Ta(OEt)_4OCH_2CH_2NHEt$	-	124 (0.10)	-	76	colourless liquid	Minor	Good
$Ta(OEt)_4OCH_2CH_2NMe_2$	-	86 (0.15)	-	> 91	colourless liquid	None	Excellent
$Ta(OEt)_4O(CH_2)_3NMe_2$	-	122 (0.08)	-	72	colourless liquid	Minor	Good
$Ta(OEt)_4OCH_2CH_2NEt_2$	-	151 (0.10)	-	69	yellow liquid	Minor	Good
$Ta(OEt)_4OCHMeCH_2NMe_2$	-	84 (0.10)	-	78	colourless liquid	Minor	Good
$Ta(OEt)_3(OCH_2CH_2NMe_2)_2$	-	129 (0.12)	-	50	colourless liquid	Substantial	Excellent
$Ta(OEt)_4acac$	-	112 (0.80)	1.50	> 80	yellow solid	Minor	Excellent
$Ta(OEt)_2(acac)_3$	36	100 (0.10)	-	56	orange liquid	Substantial	Good
$Ta(OBu^t)_4acac$	34	103 (0.15)	-	> 80	orange solid	Minor	Excellent
$Ta(OBu^t)_3(acac)_2$	-	88 (0.10)	-	55	orange liquid	Substantial	Good
$Ta(OBu^t)_2(acac)_3$	-	99 (0.11)	-	45	red-orange liquid	Substantial	Good
$Ta(OMe)_4OCH_2CH_2NMe_2$	-	90 (0.20)	1.45	90	colourless liquid	None	Good
$Ta(OSiMe_3)_4acac$	-	100 (0.10)	1.35	85	colourless liquid	Minor	Good

Decomposition of the compounds was assessed on the basis of colour after distillation, and the yield obtained. Shelf life was qualitatively assessed by observing colour change of the compound in a sealed bottle. Physical properties for selected compounds are given in Table 1.

The compounds according to the invention are suitable for use in MOCVD because they are sufficiently volatile at reduced pressure, and they provide good quality tantalum oxide deposits with relatively little contamination by carbon.

These compounds may be used as precursors for metal organic chemical vapour deposition (MOCVD) of oxide layers in applications such as integrated circuit dielectrics, microwaves, optical coatings and catalysts.

Deposition of Tantalum Oxide

A comparison was made between tantalum oxide deposited from tantalum ethoxide and from the new compound, tantalum tetraethoxydimethylaminoethoxide (compound 5 above). The new compound was found to evaporate at lower temperatures and give oxide films having improved O:Ta ratios prior to annealing. The films contained less carbon and grew at a faster rate. We ascribe the increased volatility to the monomeric nature of the new compound compared to the known dimerism of tantalum ethoxide in the vapour phase. We attribute the improved deposition characteristics to the functionalisation which permits surface attachment followed by promoted sequential loss of organic groups.

The films were grown in an Advanced Furnace Technology (Cambridge UK) Pilotrig III cold wall reactor on <100> p-type silicon at low pressure. Precursor delivery lines

were heated to avoid condensation. Table 2 below compares deposition conditions for the two selected materials. Film composition analysis was by SIMS (secondary ion mass spectroscopy) and AES (Auger electron spectroscopy).

Deposition Parameter	$Ta(OEt)_5$	$Ta(OEt)_4OCH_2OCH_2NMe_2$
Bubbler N_2 flow	100 sccm	100 sccm
Bubbler temp.	110°C	60°C
Delivery line temp.	135°C	85°C
Wafer deposition temp.	450°C	385°C
Chamber pressure	0.6 mm Hg	0.5 mm Hg
O:Ta ratio	2.35	2.46
Carbon content	6.7% at	2.3% at
Depostion rate	7 nm/min	19 nm/min

Table 2

O:Ta ratios and carbon content were measured before annealing. Bubbler flow rate is measured in standard cubic centimetres per minute (sccm).

Although the compounds have been designed particularly for use with MOCVD the invention is not limited to this use, and it will be appreciated that the compounds may also be of utility in other applications, for example vapour phase catalysis.

Because of the high solubility of the compounds in hydrocarbons they may be of use as antioxidant additives for fuels, for example in solution in a hydrocarbon and/or oil.

CLAIMS

1. A compound of the formula $Ta(OR)_{5-n}X_n$, wherein:
n is 1, 2 or 3;
each R is independently selected from a straight or branched chain alkyl group having between 1 and 4 carbon atoms, or $SiMe_3$; and
X is a bidentate ligand.

2. A compound as claimed in Claim 1, which has a distillation temperature below 160°C at a pressure of 0.1 mm Hg.

3. A compound as claimed in claim 1 or Claim 2, wherein the ligand X is the residue of an alkoxy alcohol or amino alcohol.

4. A compound as claimed in any one of the preceding claims, wherein the ligand X is a residue selected from the following:
methoxyethanol, ethoxyethanol, n-butoxyethoxyethanol; methylaminoethanol, ethylaminoethanol, dimethylamino-ethanol, diethylaminoethanol, dimethylaminopropan-2-ol and dimethylaminopropan-1-ol.

5. A compound as claimed in any one of the preceding claims, wherein the ligand X is a residue of methoxyethanol, ethoxyethanol, propoxyethanol, or butoxyethanol.

6. A compound as claimed in Claim 1 or Claim 2, wherein the ligand X is the anionic residue of a ß-diketone.

7. A compound as claimed in Claim 6, wherein the ligand X is a residue selected from:

acetylacetone, tetramethylheptanedione, trifluroacetylacetylacetone, hexafluoroacetylacetone, and diphenylacetylacetone.

8. A compound as claimed in any one of the preceding claims, wherein all R groups have the same structure.

9. A compound as claimed in claim 8, wherein R is selected from one of: methyl, ethyl, isopropyl, or t-butyl.

10. A compound as claimed in any one of the preceding claims, wherein n = 1.

11. A process for the preparation of compounds as claimed in any one of the preceding claims, which process comprises treating a tantalum compound of formula $Ta(OR)_5$ with n molar equivalents of XH.

12. A process as claimed in claim 11, which is carried out in a hydrocarbon solvent.

13. A method of chemical vapour deposition on a substrate, which method comprises heating a compound having a formula as claimed in any one of Claims 1 to 10 under reduced pressure so that the compound is transported to a heated substrate upon which it pyrolyses to form a tantalum oxide film.

14. The use of a compound as claimed in any one of Claims 1 to 10 as a precursor for tantalum oxide in a MOCVD process.

15. An article which has been at least partially coated with tantalum oxide by the method of Claim 13.

AMENDED CLAIMS

[received by the International Bureau on 28 August 1995 (28.08.95); original claim 1 amended; remaining claims unchanged (3 pages)]

1. A compound of the formula $Ta(OR)_{5-n}X_n$, wherein:
n is 1, 2 or 3;
each R is independently selected from a straight or branched chain alkyl group having between 1 and 4 carbon atoms, or $SiMe_3$; and
X is a bidentate ligand; but not the compound wherein R is ethyl, X is acetylacetanoate, and n is 3; or the compound wherein R is methyl, X is acetylacetanoate, and n is 1; or the compound wherein R is isopropyl, X is ethoxyethoxide, and n is 2.

2. A compound as claimed in Claim 1, which has a distillation temperature below 160°C at a pressure of 0.1 mm Hg.

3. A compound as claimed in claim 1 or Claim 2, wherein the ligand X is the residue of an alkoxy alcohol or amino alcohol.

4. A compound as claimed in any one of the preceding claims, wherein the ligand X is a residue selected from the following:
methoxyethanol, ethoxyethanol, n-butoxyethoxyethanol; methylaminoethanol, ethylaminoethanol, dimethylamino-ethanol, diethylaminoethanol, dimethylaminopropan-2-ol and dimethylaminopropan-1-ol.

5. A compound as claimed in any one of the preceding claims, wherein the ligand X is a residue of methoxyethanol, ethoxyethanol, propoxyethanol, or butoxyethanol.

6. A compound as claimed in Claim 1 or Claim 2, wherein the ligand X is the anionic residue of a β-diketone.

7. A compound as claimed in Claim 6, wherein the ligand X is a residue selected from:
acetylacetone, tetramethylheptanedione, trifluroacetylacetylacetone, hexafluoroacetylacetone, and diphenylacetylacetone.

8. A compound as claimed in any one of the preceding claims, wherein all R groups have the same structure.

9. A mpound as claimed in claim 8, wherein R is selected from one of: methyl, ethyl, isopropyl, or t-butyl.

10. A compound as claimed in any one of the preceding claims, wherein n = 1.

11. A process for the preparation of compounds as claimed in any one of the preceding claims,
which process comprises treating a tantalum compound of formula $Ta(OR)_5$ with n molar equivalents of XH.

12. A process as claimed in claim 11, which is carried out in a hydrocarbon solvent.

13. A method of chemical vapour deposition on a substrate, which method comprises heating a compound having a formula as claimed in any one of Claims 1 to 10 under reduced pressure so that the compound is transported to a heated substrate upon which it pyrolyses to form a tantalum oxide film.

AMENDED SHEET (ARTICLE 19)

14. The use of a compound as claimed in any one of Claims 1 to 10 as a precursor for tantalum oxide in a MOCVD process.

15. An article which has been at least partially coated with tantalum oxide by the method of Claim 13.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 95/00644

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C07F 9/00, C23C 16/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C07F, C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS-ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Progress in crystal growth and characterization, Volume 22, 1991, F. W. Ainger et al, "Deposition of ferroelectric oxides by mocvd", page 183 - line 197, see especially pages 187-188 --	1-2,6-9, 13-15
X	EP, A2, 0095094 (HITACHI, LTD.), 30 November 1983 (30.11.83), see especially page 8 --	1-2,6-10
X	US, A, 4525468 (MARK P. MACK ET AL), 25 June 1985 (25.06.85), column 3, line 40 - line 41 --	1-5,8-12

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 1995	4. 07. 95

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	GÖRAN KARLSSON

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemical Abstracts, Volume 63, No 7, 27 Sept 1965 (27.09.65), (Columbus, Ohio, USA), R. Gutet al, "Niobium (V) and tantalum (V) complexes of acetylacetone and pyrocatechol, prepared from the pentamethylates", THE ABSTRACT No 7880e, Helv. Chim. Acta 1965, 48 (92), 878-886	1-2,6-10

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INTERNATIONAL SEARCH REPORT

03/05/95

International application No.
PCT/GB 95/00644

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			JP-A-	58203443	26/11/83
			JP-B-	62028462	20/06/87
			US-A-	4510222	09/04/85
US-A-	4525468	25/06/85	US-A-	4440869	03/04/84

Form PCT/ISA/210 (patent family annex) (July 1992)